

A Study of Some Reactions Involving Free Alkyl Groups

A DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY
IN THE UNIVERSITY OF MICHIGAN

By
Loren Thomas Jones
1934

Easton, Pa.
Mack Printing Company
1934



[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

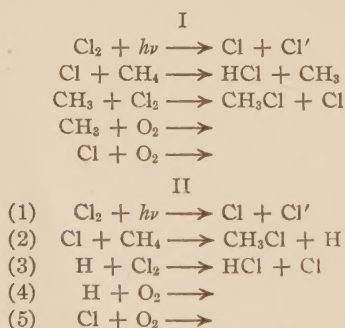
Reactions Involving Free Alkyl Groups. I. The Photo-reaction of Methane, Chlorine and Oxygen¹

BY LOREN T. JONES AND JOHN R. BATES

Studies of the thermal² and photochemical³ chlorination of methane have shown that in both cases the reaction proceeds by a chain mechanism. Coehn and Cordes found a quantum yield of 10^4 while the work of Pease and Walz indicated a much greater chain length for higher temperatures. Both reactions are strongly inhibited by traces of oxygen. The analogy between these data and the facts of the hydrogen-chlorine reaction immediately suggests that the reaction occurs through the same intermediates which characterize the hydrogen-chlorine reaction, with methyl groups taking the place of one of the hydrogen atoms of the hydrogen molecules. If this be true, the rate should obey the expression derived by Thon⁴ with substitutions

$$\frac{d[\text{CH}_3\text{Cl}]}{dt} = \frac{d[\text{HCl}]}{dt} = \frac{K [\text{CH}_4][\text{Cl}_2]^2}{[\text{O}_2] (k [\text{CH}_4] + [\text{Cl}_2])}$$

This would be equally true were the mechanism to follow either of the two alternative schemes



Measurements accordingly have been made to discover if this is true, and, in addition, the verification of either I or II as the correct interpretation has been attempted.

(1) The material in this paper comprises a portion of a thesis presented by Loren T. Jones to the Graduate School of the University of Michigan in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1934.

(2) Pease and Walz, *THIS JOURNAL*, **53**, 3728 (1931).

(3) Coehn and Cordes, *Z. physik. Chem.*, **B9**, 1 (1930).

(4) Thon, *ibid.*, **B9**, 1 (1930).

Experimental Method

The experiments were carried out in a flow system. The rate of flow of the methane and chlorine supplied in tanks was measured by pressure flowmeters. The amount of oxygen, generated electrolytically, was regulated by the current sent through the cell. The gases were mixed and dried in a drying tower before entering the reaction unit consisting of a glass spiral illuminated by a Pyrex mercury arc. Since traces of oxygen have a very marked influence on the reaction at low oxygen concentrations, an analysis of the methane and chlorine for oxygen content was made. Approximately 3000 cc. of chlorine, when bubbled into a bulb filled with an iodide solution, gave about 30 cc. of residual gas. This was transferred to an Orsat gas analysis apparatus where the gas was first bubbled through an alkali solution to remove any traces of chlorine or other acidic gases that might be present before absorbing the oxygen in an alkaline hydrosulfite solution. There was found 0.25% oxygen in the chlorine and 0.8% in the methane. The reaction was studied by determining the amount of hydrogen chloride and unreacted chlorine in the off-gas by absorbing it in an iodide solution. The iodine liberated was titrated with a thiosulfate solution; the acid formed during the reaction was determined with alkali.

The reaction was carried out at 5, 25 and 45° at atmospheric pressure. A series of determinations was first made in which the methane-chlorine-oxygen ratio was constant, as the total rate of flow was increased from 135 cc. per minute to 370 cc. per minute.

The amount of hydrogen chloride formed after a ten-minute run remained constant within 10%; as can be seen from Table I.

Since there is a possibility of fluctuation of light intensity, a check was made at frequent intervals

TABLE I

CH ₄ , cc./min.	Cl ₂ , cc./min.	O ₂ , cc./min.	Total, cc./min.	% HCl formed	HCl formed, cc./min.
80	56	2.10	135	5.51	2.83
110	80	3.00	193	3.60	2.85
185	115	4.75	305	2.10	2.75
215	155	6.80	377	1.50	2.64

using an arbitrarily chosen concentration for each of the different series.

Experimental Results

In Fig. 1 the change in hydrogen chloride with oxygen increase is plotted for various methane-chlorine ratios at 25°. The dependence of the reaction rate on the low oxygen concentration shows up very decidedly. As would be expected if the reaction mechanism agrees with that of the hydrogen, chlorine and oxygen, the greater the chlorine concentration the greater will be the rate of formation of hydrogen chloride. The methane-chlorine concentrations were varied from a 3 to 1, to a 1 to 2 ratio.

The data are given in Tables II and III. Table II contains a typical set of measurements, the italicized values being the check run. Table III consists of a summary of all the runs for different methane-chlorine ratios and different temperatures. The first two columns give the average methane and chlorine concentrations for

a number of runs (as in Table II). Next come two pairs of oxygen-hydrogen chloride values, these being minimum and maximum oxygen values with the corresponding amount of hydrogen chloride formed. Runs B at 5° were obtained using a new spiral which gave larger values for hydrogen chloride and K , but when converted on the basis of the check run (using a factor of 0.565 for K) gave good agreement with the other experiments.

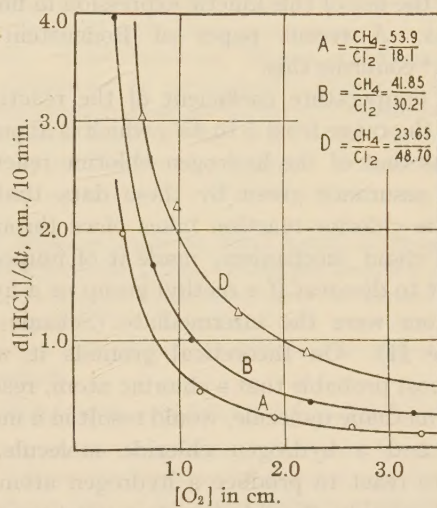


Fig. 1.

The values of K given in the table are calculated from Thon's equation, giving k values of 10, 1 and 0.1. As can be seen constancy of K with variations in the methane-chlorine ratio can be obtained only if $k = 1$, instead of 10 as in the hydrogen-chlorine reaction.

Since Thon's work was carried out in a static system, runs of the hydrogen-chlorine-oxygen reaction were made in our flow system to be sure that the equation might be applied to the present

TABLE II
Reaction at 25°

CH ₄ , cm.	Cl ₂ , cm.	O ₂ , cm.	HCl, cm.	K		
				$k = 10$	$k = 1$	$k = 1/10$
42.5	31.1	0.386	3.93	0.0163	0.00272	0.00126
55.0	18.5	.451	1.97	.0269	.00348	.00114
54.3	18.2	1.18	0.549	.0202	.00262	.00085
53.9	18.1	1.91	.312	.0188	.00243	.00079
53.6	18.0	2.63	.230	.0193	.00249	.00081
52.9	17.8	3.32	.160	.1074	.00225	.00070
				.0205	.00265	.00086

TABLE III
Reaction at 25°

	CH ₄ , cm.	Cl ₂ , cm.	O ₂ , cm.	HCl, cm.	O ₂ , cm.	HCl, cm.	K		
							$k = 10$	$k = 1$	$k = 1/10$
A	53.90	18.10	0.451	1.97	3.32	0.160	0.0205	0.00265	0.00086
B	41.85	30.21	.349	3.95	3.23	.331	.0139	.00228	.00109
C	37.05	35.35	.308	4.67	3.19	.518	.0145	.00255	.00139
D	23.65	48.70	.628	3.04	2.20	.888	.0096	.00245	.00173

Reaction at 45°

A	54.95	17.90	.441	2.12	2.42	.255	.0226	.00294	.00094
B	41.53	31.25	.431	4.33	3.68	.382	.0174	.00285	.00137
C	25.50	47.15	.735	3.40	2.27	.925	.0112	.00270	.00184

Reaction at 5°

A	54.0	18.7	.500	1.47	2.39	.255	.0195	.00249	.00083
B	43.2	29.5	.534	4.15	2.74	.853	.0157	.00243	.00113

work. The results of these are summarized in Table IV.

TABLE IV

H ₂ , cm.	Cl ₂ , cm.	O ₂ , cm.	HCl, cm.	K
44.0	30.0	0.32	17.8	0.067
43.6	29.7	1.048	5.44	.065
43.0	29.3	1.79	3.32	.073
42.3	28.6	3.08	2.02	.074

As can be seen, K is sufficiently constant to justify the use of this kinetic expression in flowing systems. A recent paper of Bodenstein and Schenk⁵ confirms this.

The temperature coefficient of the reaction is 1.1 for the range from 5 to 45°, which is about the same as that of the hydrogen-chlorine reaction.⁶

The assurance given by these data that the methane-chlorine reaction takes place through a Nernst chain mechanism, made it of immediate interest to discover if a methyl group or a hydrogen atom were the intermediate (Scheme I or Scheme II). On theoretical grounds it would seem most probable that a chlorine atom, reacting with a methane molecule, would result in a methyl group and a hydrogen chloride molecule. In order to react to produce a hydrogen atom and methyl chloride, the chlorine atom must approach one of the triangular faces of the "carbon tetrahedron," where the residual bond forming power of the carbon atom has its greatest value.⁷ Here it would be in interaction with the three hydrogen atoms situated on the apices of the triangle, resulting in a strong repulsion which would tend to necessitate a high activation energy. If, however, the chlorine atom approached along the line of the carbon hydrogen bond, it might react

with the hydrogen atom with a much lower activation energy, since it would be separated by larger distances from the other three hydrogen atoms.

Experimentally, attempts to differentiate between the two possibilities failed. The hydrogen atoms, if formed, would undoubtedly yield hydrogen peroxide,⁸ which may be detected in the presence of chlorine by the colorimetric method using titanium. No color was obtained after bubbling the off-gases, in which there was a large oxygen content, for an hour through an acidified solution of titanium chloride.

A number of different methods were used to try to remove the excess of chlorine which makes ineffective the usual tests for the extremely small amounts of formaldehyde which must be present. Fractional distillation, passing the gas over ascarite, mercury-zinc amalgam, and reducing the chlorine by a stannous chloride solution all failed to give a solution or a gas which would yield confirmatory evidence for the presence of formaldehyde. The tests employed were the resorcinol ring, formation of the *p*-nitrophenylhydrazone and the ultraviolet absorption spectrum of the gas.

Summary

The photoreaction between methane and chlorine obeys the equation of Thon for the inhibiting effect of oxygen. The reaction must therefore take place through a Nernst chain mechanism. Whether the methyl group or hydrogen atom is the chain carrier could not be verified experimentally, although simple considerations of the collision mechanism of a chlorine atom and a methane molecule make the former seem more probable.

ANN ARBOR, MICHIGAN

RECEIVED JULY 24, 1934

(5) Bodenstein and Schenk, *Z. physik. Chem.*, **B20**, 420 (1933).

(6) Porter, Bardwell and Lind, *THIS JOURNAL*, **48**, 2603 (1926).

(7) Pauling, *ibid.*, **53**, 1367 (1931); Slater, *Phys. Rev.*, **37**, 381 (1931).

(8) Bates and Salley, *THIS JOURNAL*, **55**, 110 (1933).

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

Reactions Involving Free Alkyl Groups. II. The Photo-oxidation of Gaseous Ethyl Iodide¹

BY LOREN T. JONES AND JOHN R. BATES

In a previous investigation it was shown that the photo-reaction which methyl iodide undergoes in the presence of oxygen is essentially the oxidation of free methyl groups.² A similar reaction with ethyl iodide should yield the same data for ethyl groups and the present work concerns itself with an attempt to compare the reactions of the two different alkyl groups. Bates and Spence have already found that the products of the ethyl iodide-oxygen reaction are iodine, acetaldehyde and ethyl alcohol, which are analogous to the products of the methyl iodide reaction. More recently Thompson and Kelland³ attempted a similar study by studying the oxidation of zinc diethyl. There was ample evidence, however, that free ethyl groups were not intermediates in this reaction.

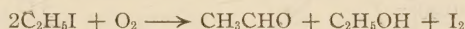
Experimental Method

The experimental arrangement consisted of a quartz reaction vessel joined by capillary tubing to a mercury manometer and oil pump. The vessel was clear fused quartz, 50 mm. in diameter, 150 mm. in length and having a volume of 268 cc. with two plane, circular, polished windows fused into either end. This was fitted into a metal tank in such a way that one window was flush with the outer side of the tank. As the vapor pressure of ethyl iodide at 0° is too low to give a workable range of pressures, it was necessary to work at a higher temperature. This was accomplished by circulating water, thermostatically regulated at 17 ± 0.3°, into the tank so the vessel was completely covered. The iodine condensed on the sides rather than the window illuminated. Its vapor pressure is 0.158 mm. at 17° as calculated from the equation given by Giauque.⁴ Ethyl iodide was first treated with sodium bisulfite solution to remove the iodine, separated from the aqueous layer, and dried with calcium chloride before distillation. Only the colorless portion boiling between 72-73° was reserved which was redistilled, *in vacuo*, into a storage bulb and kept under its own pressure as a practically colorless liquid. Tank oxygen, dried by calcium chloride, was kept in a large bulb from which it could be introduced into the reaction vessel. A mercury vapor lamp of the Kromayer type was the source

of illumination, arranged so that after tilting to start the arc, it could be returned to the same place each time.

The Action of Light on Ethyl Iodide Vapor in the Absence of Oxygen.—When pure ethyl iodide vapor is illuminated for long periods of time no decrease in pressure is observed and only a small amount of iodine is liberated. As an illustration, 120 mm. of the vapor, upon being illuminated for seven hours, showed no pressure decrease, yet a residual gas pressure of approximately 8 mm. remained when the trap of the vessel was immersed into a carbon dioxide-ether mixture. The iodine liberated was equivalent to a decrease of 8.1 mm. of ethyl iodide.

The Action of Light on Ethyl Iodide in Presence of Oxygen.—With the presence of oxygen there is a pressure decrease which is sufficiently rapid to permit kinetic measurements. The iodine liberated was titrated and the pressure decrease was calculated on the basis of the all-over reaction



in which the initial pressure is decreased by one third. Table I shows the experimental decrease and that calculated on the basis of the above equation from the iodine liberated.

TABLE I

$\text{C}_2\text{H}_5\text{I}$, mm.	O_2 , mm.	0.121 N $\text{Na}_2\text{S}_2\text{O}_3$, cc.	$-\Delta P$ obs.	$-\Delta P$ calcd.
53	304	2.03	9.0	8.10
50	300	1.51	6.2	6.79
50	293	1.72	8.4	7.97
50	13.8	1.00	4.8	4.05
55	12.4	1.04	4.8	4.21
50	23.4	0.81	3.6	3.25
50	27.0	1.07	4.6	4.33
52	156	0.97	4.8	4.0
52	157	.96	4.2	4.0

Variations of Ethyl Iodide and Oxygen Concentrations.—

An endeavor to maintain uniform light intensity for each series of experiments, and constant conditions for all the series were made in every one of the kinetic measurements. The uniformity of light intensity was checked by repeating one of the experiments chosen as a reference point, and if no change in rate was observed, it was assumed that the light intensity had remained constant. When there was an appreciable deviation, that series was discarded. Manometer readings were made at one, two or three minute intervals for about seven to ten minutes duration. After ten to fifteen minutes, depending upon concentrations, the rate would decrease appreciably, so measurements were made for that part that gave a linear relationship between pressure decrease and time. At the beginning of each run a small expansion, known as the Budde effect, similar to that shown by methyl iodide and

(1) The material in this paper comprises a portion of a thesis presented by Loren T. Jones to the Graduate School of the University of Michigan in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1934.

(2) Bates and Spence, *THIS JOURNAL*, **53**, 1689 (1931); *Trans. Faraday Soc.*, **27**, 414 (1931).

(3) Thompson and Kelland, *J. Chem. Soc.*, 756 (1933).

(4) Giauque, *THIS JOURNAL*, **53**, 507 (1931).

chlorine upon illumination was observed. Figure 1 contains results obtained upon varying the concentrations

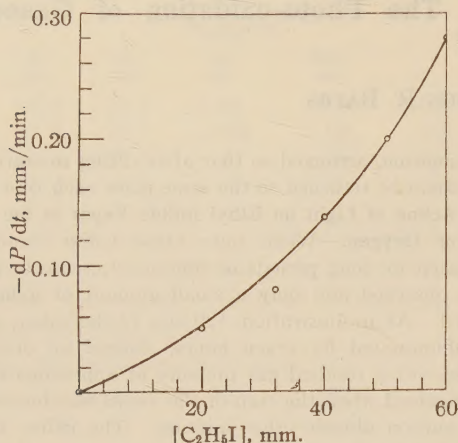


Fig. 1.

of ethyl iodide and constant oxygen. The results for varying the oxygen concentrations and constant ethyl iodide are given in Fig. 2.

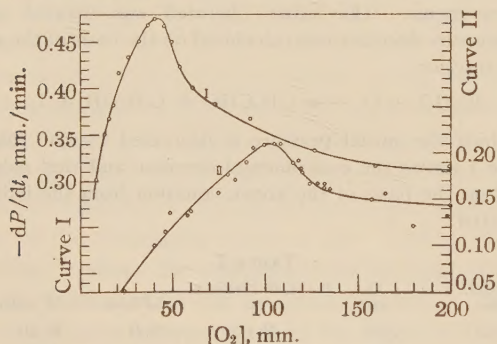
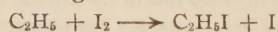
I [C₂H₅I] = 75 mm., II [C₂H₅I] = 50 mm.

Fig. 2.

Theoretical Discussion

Decomposition of Ethyl Iodide.—The decomposition of ethyl iodide in the absence of oxygen is quite similar to that of the methyl compound. The slowness of the reaction may be accounted for on the same basis. The ethyl groups, once formed, react for the most part with iodine, regenerating the iodide.



Some few apparently react according to the equation



There is thus no resulting pressure change, which would be the case were they to combine to form butane.

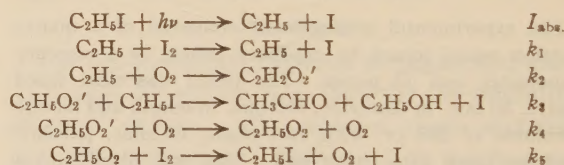
Their reaction with disproportionation is further indicated by the results of Emschwiller,⁵ who found in the liquid photo-reaction ethylene and

(5) Emschwiller, *Compt. rend.*, **192**, 799 (1931).

ethane, but neither butane nor hydrogen. This is also analogous to the reaction suggested to explain the reaction of hydrogen atoms with oxygen and other molecules⁶ where the intermediate HO₂ molecules react for the most part with disproportionation.



Ethyl Iodide and Oxygen.—The change in the rate of the oxidation reaction with oxygen and with ethyl iodide concentrations is entirely unlike the methyl group oxidation. The appearance of the maximum rate with increasing oxygen concentration (Fig. 2) and the very rapid increase in rate with increasing ethyl iodide concentration (Fig. 1) indicate that the simple mechanism postulated for the methyl group cannot be applied here. It is evident that only through a peroxide intermediate will it be possible to obtain the maximum in the rate-oxygen curve. Another fact which is apparent from an inspection of the curves in Fig. 2 is that at high oxygen concentrations an asymptote greater than zero is approached. This removes the possibility of explaining the results with the simpler of the peroxide mechanisms

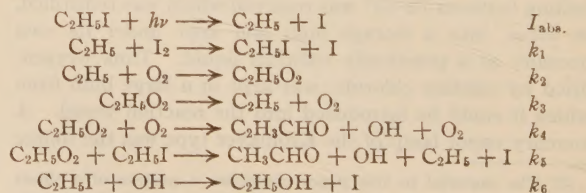


where C₂H₅O₂' represents the energy rich peroxide upon formation. This yields as a rate expression

$$-\frac{d[\text{C}_2\text{H}_5\text{I}]}{dt} = \frac{2I_{\text{abs}}k_2k_3[\text{C}_2\text{H}_5\text{I}][\text{O}_2]}{(k_1[\text{I}_2] + k_2[\text{O}_2])(k_3[\text{C}_2\text{H}_5\text{I}] + k_2[\text{O}_2])}$$

which contains an [O₂]² term in the denominator and gives a maximum, with appropriate choice of constants. However, at high [O₂] the curve will approach zero, which does not coincide with experiment.

A scheme which gives a fairly satisfactory representation of the data is



$$-\frac{d[\text{C}_2\text{H}_5\text{I}]}{dt} = \frac{2I_{\text{abs}}[\text{O}_2]k_2(k_4[\text{O}_2] + k_5[\text{C}_2\text{H}_5\text{I}])}{k_2k_4[\text{O}_2]^2 + k_1k_4[\text{I}_2][\text{O}_2] + k_1k_3[\text{I}_2] + k_1k_5[\text{C}_2\text{H}_5\text{I}][\text{I}_2]}$$

(6) Bates, *J. Chem. Phys.*, **1**, 457 (1933).

This expression will give a curve representing the change in reaction rate with oxygen concentration which is of the same general form as the experimental results. It was, however, found to be impossible to fit the experiments with any degree of exactness. With numerical constants assigned to the constant terms appearing in the theoretically derived expression it was found that an agreement for low oxygen concentrations gave values which were systematically at variance with the portion of the experimental curve representing the results at high concentrations. Comparison is made by using the empirical equation

$$-\frac{d \text{C}_2\text{H}_5\text{I}}{dt} = \frac{a [\text{O}_2]^2 + b [\text{O}_2]}{[\text{O}_2]^2 + c [\text{O}_2] + d}$$

Values may be assigned to the constants in order to calculate the rate. For the ethyl iodide concentration constant at 50 mm. the values $a = 0.1$, $b = 16$, $c = 7$ and $d = 3,700$ gave the best agreement; at 75 mm. the values $a = 0.16$, $b = 60$, $c = 75$ and $d = 1,200$ were found best.

The deviations may be due to a systematic error in the experimental results or to the fact that the reaction is more complex than we have considered. We believe that such an error cannot be considered plausible in the light of reproducibility of the results.

The change in rate with ethyl iodide can be seen to be in agreement with this equation when it is remembered that $I_{\text{abs.}}$ is a function of the iodide, thus giving a total dependence of the rate on ethyl iodide of a power lying between one and two, depending upon the value of the absorption coefficient of ethyl iodide.

Although by considering other more complex reaction schemes an expression can be found which

fits the results, with an appropriate choice of constants, we feel that the significance of such expressions is defeated by their complexity and therefore prefer to leave the question open, pending either a more simple explanation or a much more extensive investigation.

It may, however, be inferred quite definitely from the results of the present work that a peroxide is an intermediate in ethyl group oxidation, since only by such an assumption may any sort of agreement be obtained with experiment. Such peroxides have been found to be quite generally necessary for the interpretation of oxidation processes involving hydrocarbons as well as other atoms and radicals.⁷

Summary

The photodecomposition of ethyl iodide is extremely slow, resulting after long periods of illumination in an uncondensable gas which is probably ethylene and ethane.

The oxidation is rapid, giving rise to a pressure decrease which indicates acetaldehyde and ethyl alcohol as end-products. The rate of oxidation increases to a maximum, with increasing oxygen content, and then falls off to an asymptotic value greater than zero. The results can be interpreted to a certain degree of exactness by a mechanism involving an intermediate ethyl peroxide, but small deviations from theory indicate a great complexity. A peroxide, however, is the only intermediate which will give even an approximate agreement, which is in accord with other oxidation processes.

ANN ARBOR, MICHIGAN

RECEIVED JULY 24, 1934

(7) Thompson and Kelland, *J. Chem. Soc.*, 756 (1933); Bodenstein, *Z. physik Chem.*, **B11**, 1516 (1931).

Digitized by the Internet Archive
in 2026

